SUPPORTING INFORMATION

Catalytic hydroxylation of benzene and toluene by an iron complex bearing a chelating di-pyridyl-di-NHC ligand

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Experimental Procedures

General. All chemicals were purchased from commercial suppliers and used without further purification if not otherwise noted. Complex **1** was synthesized according to the literature procedure.^[1] Acetonitrile (HPLC grade), H_2O_2 (30 wt.-% in H_2O ; non-stabilized), triphenylphosphine (99 %), benzene (HPLC grade) and toluene (HPLC grade) were obtained from Acros Organics. Benzene-*d6* and toluene-*d8* were purchased from Eurisotop. GC-FID/MS measurements were performed on a Varian CP-3800 equipped with a Optima Waxplus column (FID; 0.50 µm; 30 m·0.32 mm) or a FactorFour VF-200ms column (MS; 0.25 µm; 30 m·0.25 mm).

Standard conditions for catalytic reactions. In a typical catalytic reaction, the catalyst (5.0 mg, 1 equiv.) was dissolved in acetonitrile (2 mL) and the aromatic compound (100 equiv.) was added. H_2O_2 solution (30 % in water, 100 equiv.) was added directly under constant stirring. The reaction was quenched after 1 h with an excess of solid PPh₃ and

filtrated over a short plug of silica to remove metal impurities. An external standard solution in MeCN was added to the reaction solution (equal volumes) and quantified by GC-FID/MS. In the case of benzene hydroxylation, fluoro-benzene (standard for benzene) and 4-bromoanisole (standard for phenol) was used as standard, and in the case of toluene hydroxylation mesitylene (standard for toluene) and 4-bromo-anisole (standard for all oxidation products) were used. The samples were quantified via a multipoint calibration with excellent reproducibility. All experiments were repeated at least twice.

Catalytic aromatic oxidations were carried out in an open small vial under atmospheric conditions. To exclude the influence of air, catalysis was also performed under Argon atmosphere with no influence on the activity. Furthermore, no influence of the filtration or PPh₃ quenching on the reaction was observed when non-filtrated or non-quenched samples were measured.

Catalytic experiments in varied conditions. For reactions with different amounts of H_2O_2 or different molarities, the amount of H_2O_2 or solvent was adapted. The temperature dependent catalytic reactions were carried out using a cryostat in a cooling bath with through flow of the coolant. The temperature of the reaction mixture was allowed to equilibrate for at least 15 min prior to the addition of H_2O_2 . Kinetic isotope effects were determined under typical reaction conditions similar to a previously described method, and quantified through gas chromatography.^[2]

Entry	T [°C]	Conv. [%]	Sel. [%]	Yield [%]
1	60	15.1	36.4	5.5
2	50	13.6	43.3	5.9
3	40	10.7	58.8	6.3
4	30	10	83.5	6.8
5	25	7.4	93.6	6.9
6	10	7.0	94.2	6.6
7	0	4.4	98.2	4.2

Table S1. Influence of the reaction temperature on the catalytic oxidation of benzene to phenol.

Reaction conditions: 5mg of **1** in 2 mL of MeCN (3.2 mM), 61 μ L bezene (100 equiv), 70 μ L H₂O₂ (100 equiv.); reaction time: 1 h; reaction is started with the addition of H₂O₂.

References

- [1] A. Raba, M. Cokoja, S. Ewald, K. Riener, E. Herdtweck, A. Pöthig, W. A. Herrmann, F.
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- [2] E. V. Kudrik, A. B. Sorokin, Chem. Eur. J. 2008, 14, 7123-7126.